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## Description

### Background of the invention

The present invention relates to a fuel cell of the type set forth in the pre-characterisation part of claim 1.

A methanol fuel cell of this type is disclosed in U.S. patent specification No. 4,262,063.

The prior art methanol fuel cell has not yet attained satisfactory cell performance and high utilisation efficiency of the methanol.

### Summary of the invention

It is the object of the present invention to provide a methanol fuel cell of the above type which has a good cell performance, especially a high cell voltage, and which exhibits increased utilisation efficiency of the methanol.

This object is met by a methanol fuel cell as defined in claim 1. The invention is based on the finding that, by placing a plurality of ion-exchange films one over another, the effect of suppressing the volume of methanol that permeates through the cation-exchange films in other words, the fuel suppressing effect can be enhanced, thereby increasing the fuel utilisation efficiency.

### Brief description of the drawings

Figure 1 is a sectional view of a methanol fuel cell showing an embodiment of the present invention.

Figure 2 is a graph illustrative of the relationship between the methanol permeability coefficient of a cation-exchange resin film and the cell voltage in the methanol fuel cell shown in Figure 1.

Figure 3 is a graph illustrative of the relationship between the methanol permeability coefficient of the cation-exchange resin film and the methanol utilization efficiency in the methanol fuel cell shown in Figure 1.

Figure 4 is a graph illustrative of the relationship between the number of cation-exchange resin films and the methanol permeation volume of the film(s) as well as the electric resistance of the film(s), in the methanol fuel cell shown in Figure 1.

Figure 5 is a graph illustrative of the relationship between the number of the cation-exchange resin films and the voltage drop of the cell in the methanol fuel cell shown in Figure 1.

### Preferred embodiments of the invention

Referring to Figure 1, a methanol fuel cell according to the present invention is constructed of a methanol electrode (negative electrode) 1, an oxidation electrode (positive electrode) 2, cation-exchange resin films (hydrogen ion- and/or hydronium ion-conductive solid films) 31, 32 and 33, an electrolyte (anolyte) 4 which contains 3 mol/l of sulfuric acid and 1 mol/l of methanol, a cell case 5, a supply port 6 for the electrolyte, an exhaust port 7 for carbonic acid gas, an oxidant chamber 8 into which the air, oxygen or the like is

supplied, a supply port 9 for the oxidant such as air and oxygen, and an exhaust port 10 for the oxidant or for the oxidant and water vapour.

According to the present invention, the cation-exchange resin films 31 to 33 are set at a methanol permeability coefficient of at most

$$1 \times 10^{-6} \text{ mol/(mol/l) \cdot min \cdot cm}^2.$$

Thus, as will be described later, it is possible to obtain high cell voltage and good utilization efficiency of methanol [that is, the proportion of the quantity of electricity (ampere-hour or coulomb) which can be actually derived from the methanol, with respect to the quantity of electricity which can be theoretically derived from the methanol].

These effects are similarly brought forth in a cell of the so-called laminated structure in which several unit cells are combined.

Cells of the construction shown in Figure 1 were assembled by the use of sulfonic acid type cation-exchange resin films having various methanol permeability coefficients (e.g., a film of 'Nafion 425' produced by Du Pont de Nemours, which is known as one for electrodialysis, which contains a fluorocarbon resin as its main component and which has an electric resistance of approximately  $0.5 \Omega \cdot \text{cm}^2$ ). As each of the air electrode (positive electrode) and the methanol electrode (negative electrode), a tantalum gauze having a size of  $95 \text{ mm} \times 140 \text{ mm}$  was coated with  $20 \text{ mg/cm}^2$  of platinum black agglomerated by employing polytetrafluoroethylene as a binder. The thickness of each electrode was 1 mm. Diaphragms (ion-exchange films) each being 0.1 to 0.5 mm thick were interposed between the positive and negative electrodes, and they were placed in close contact with each other into one unit cell. The methanol in the anolyte decomposed on the negative electrode 1 to produce hydrogen ions. The hydrogen ions turned into water by passing through the diaphragms (ion-exchange films) and reacting with oxygen in the air in the positive electrode 2. The water was exhausted through the exhaust port 10. When the methanol decomposed, it emitted electrons, which reached the positive electrode through an external circuit, thus producing electric energy.

The above cells were subjected to a discharge experiment under the following conditions:

Current density:  $40 \text{ mA/cm}^2$ .

Temperature:  $60^\circ\text{C}$ .

The result of the experiment is shown in Figure 2.

As apparent from Figure 2, the cell voltage rises abruptly and a good discharge characteristic is exhibited on the smaller-coefficient side bordered at the methanol permeability coefficient of approximately

$$1 \times 10^{-6} \text{ mol/(mol/l) \cdot min \cdot cm}^2.$$

This is a quite unforeseen result.

In the cell of the above example, the methanol utilization efficiency in the case of employing the cation-exchange resin films with the methanol permeability coefficient of

$$1 \times 10^{-6} \text{ mol}/(\text{mol/l}) \cdot \text{min} \cdot \text{cm}^2$$

and discharging the cell at a current density of 60 mA/cm<sup>2</sup> and a temperature of 60°C is about 60% as shown in Figure 3.

The inventors studied also on the electric resistance of the cation-exchange resin films. As a result, they have found out that, with an electric resistivity of at most 0.7 Ω · cm<sup>2</sup>, the ion-exchange resin films can be prevented from changing in shape and in quality. When the films have a high electric resistance, they change in shape or in quality due to a temperature rise thereof on account of the generation of heat. In case of employing films with a resistance of 1 Ω · cm<sup>2</sup>, the rate of heat generation per cm<sup>2</sup> is 0.22 J/min. Supposing that the specific heat of the films having a thickness of 0.1 mm and an area of 1 cm<sup>2</sup> is 0.04 J, the temperature rise thereof per minute becomes 5°C. Since most of cation-exchange resin films change in shape and in quality at about 90°C, the temperature rise should desirably be suppressed to below 80°C. The inventors have experimentally verified that, because of heat radiation, it takes 10 minutes or more until the film temperature rises to 90°C. It has been experimentally verified that when the film resistance is at most 0.7 Ω · cm<sup>2</sup>, the temperature rise per minute is 3.5°C, the film temperature not rising to 80°C or above owing to heat radiation.

The methanol permeability coefficient and electric resistance of the cation-exchange resin film of the prior-art methanol fuel cell were

$$2 \times 10^{-6} \text{ mol}/(\text{mol/l}) \cdot \text{min} \cdot \text{cm}^2$$

and 0.5—0.7 Ω · cm<sup>2</sup>, respectively. The cell voltage and the methanol utilization efficiency were 0.4 V and 50%, respectively.

It has been experimentally verified that, as indicated by following expression given below and by characteristic A in Figure 4, the methanol permeation volume Q decreases in inverse proportion to the square of the number N of the ion-exchange films 31, 32, 33 etc.

$$Q = \frac{S \cdot T \cdot \Delta C}{N^2}$$

where

Q: volume of the liquid fuel to permeate through the ion-exchange films.

P: permeability coefficient.

S: area of the ion-exchange films.

T: elapsed time.

ΔC: fuel concentration difference between both the sides of the ion-exchange films.

N: number of the ion-exchange films placed one over another.

On the other hand, the electric resistance increases in proportion to the number of the ion-exchange films as indicated by characteristic B in Figure 4.

When the methanol reaches the cathode (air electrode) 2, it reacts with oxygen, and hence, the potential of the air electrode 2 lowers. The relationship between the number of the ion-exchange films and the cell voltage is illustrated as characteristic A in Figure 5.

When the number of the ion-exchange films is increased, the drop of cell voltage decreases. This is because the cation-exchange films 31, 32 and 33 prevent the methanol from reaching the cathode 2.

As another cause for the drop of the cell voltage, there is considered the resistance of the ion-exchange films 31, 32 and 33 themselves. The relationship between the number of the ion-exchange films and the drop of the cell voltage ascribable to the film resistance is illustrated as characteristic B in Figure 5.

The main causes for the drop of the cell voltage are the two causes mentioned above. The combined drop value of the cell voltage ascribable to the two becomes as indicated by characteristic C in Figure 5.

It has been experimentally verified that, in case of placing more than two films of 'Nafion 425' (produced by Du Pont de Nemours) one over the other as the cation-exchange films, the drop of the cell voltage becomes least. In this case, a value of 0.2—0.5 mm is the optimum as the thickness of the whole lamination of the cation-exchange films 31, 32, and 33.

In case of placing the cation-exchange films 31, 32, and 33 one over the other, air bubbles must be prevented from getting between these cation-exchange films. The reason is that when an air bubble is enclosed, the resistance of the whole lamination increases, resulting in a cell voltage drop. In order to prevent such air bubbles, it is more preferable that the cation-exchange films 31, 32 and 33 are placed one over the other in an acid or neutral solution, favorably a methanol solution, whereupon the resulting lamination is brought into close contact with the electrodes 1 and 2.

#### Claims

1. A methanol fuel cell comprising
  - a positive electrode (2) which has two major surfaces, a first major surface lying in direct contact with an oxygen-containing gas;
  - a hydrogen ion- and/or hydronium ion-conductive solid film (3) which has two major surfaces, a first major surface lying in close contact with the second major surface of said positive electrode (2);
  - a negative electrode (1) which has two major surfaces, a first major surface lying in close contact with the second major surface of said solid film (3); and
  - methanol fuel (4) disposed in direct contact

with the second major surface of said negative electrode (1);

characterised in that a laminate of at least two ion-exchange films sufficient to reduce the methanol permeability coefficient to at most

$$1 \times 10^{-6} \text{ mol}/(\text{mol/l}) \cdot \text{min} \cdot \text{cm}^2$$

is used as said ion-conductive solid film (3).

2. The cell of claim 1, wherein said solid film (3) has an electric resistance of at most  $0.7 \Omega \cdot \text{cm}^2$ .

3. The cell of claim 1 or 2, wherein said solid film (3) has a thickness of 0.1 to 0.5 mm.

4. The cell of any of claims 1 to 3, wherein the films (31...33) forming said laminate are placed in close contact within an acid or neutral solution.

5. The cell of any of claims 1 to 3, wherein the films (31...33) forming said laminate are placed in close contact within a solution containing methanol.

#### Patentansprüche

1. Methanol-Brennstoffzelle, umfassend eine positive Elektrode (2) mit zwei Hauptoberflächen, von denen eine erste in direktem Kontakt mit einem sauerstoffhaltigen Gas steht;

einen wasserstoffionen- und/oder hydroniumionen-leitfähigen festen Film (3) mit zwei Hauptoberflächen, von denen eine erste in engem Kontakt mit der zweiten Hauptoberfläche der positiven Elektrode (2) steht;

eine negative Elektrode (1) mit zwei Hauptoberflächen, von denen eine erste in engem Kontakt mit der zweiten Hauptoberfläche des festen Films (3) steht; und

Methanol-Brennstoff (4), der in direktem Kontakt mit der zweiten Hauptoberfläche der negativen Elektrode (1) angeordnet ist,

dadurch gekennzeichnet, daß als ionenleitfähiger fester Film (3) ein Laminat aus mindestens zwei Ionenaustauschfilmen verwendet wird, die ausreichen, um den Methanol-Permeabilitätskoeffizient auf höchstens

$$1 \times 10^{-6} \text{ Mol}/(\text{Mol/l}) \cdot \text{min} \cdot \text{cm}^2$$

herabzusetzen.

2. Zelle nach Anspruch 1, wobei der feste Film (3) einen elektrischen Widerstand von höchstens  $0,7 \Omega \cdot \text{cm}^2$  aufweist.

3. Zelle nach Anspruch 1 oder 2, wobei der feste Film (3) eine Dicke von 0,1 bis 0,5 mm hat.

4. Zelle nach einem der Ansprüche 1 bis 3, wobei die das Laminat bildenden Filme (31...33)

in engem Kontakt mit einer sauren oder neutralen Lösung angeordnet sind.

5. Zelle nach einem der Ansprüche 1 bis 3, wobei die das Laminat bildenden Filme (31...33) in engem Kontakt mit einer Methanol enthaltenden Lösung angeordnet sind.

#### Revendications

1. Pile à combustible au méthanol, comportant

— une électrode positive (2) qui comporte deux surfaces principales, une première surface principale étant en contact direct avec un gaz contenant de l'oxygène;

— une pellicule solide (3) conductrice pour les ions hydrogène et/ou pour les ions hydronium et qui comporte deux surfaces principales, une première surface principale étant en contact intime avec la seconde surface principale de ladite électrode positive (2);

— une électrode négative (1), qui comporte deux surfaces principales, une première surface principale étant en contact intime avec la seconde surface principale de ladite pellicule solide (3); et

— un combustible au méthanol (4), qui est en contact direct avec la seconde surface principale de ladite électrode négative (1), caractérisée en ce qu'on utilise, pour constituer ladite pellicule solide (3) conductrice pour les ions, un ensemble stratifié formé d'au moins deux pellicules échangeuses d'ions, qui sont suffisantes pour réduire le coefficient de perméabilité au méthanol à, au plus,

$$1 \times 10^{-6} \text{ mole}/(\text{mole/l}) \cdot \text{mn} \cdot \text{cm}^2.$$

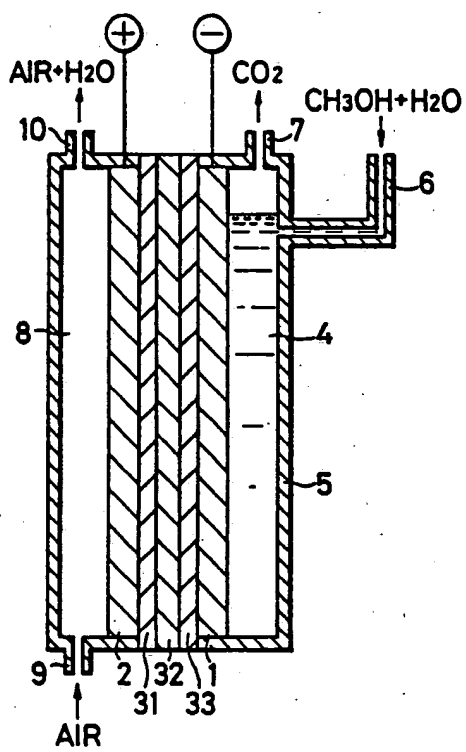
2. Pile selon la revendication 1, dans laquelle ladite pellicule solide (3) possède une résistance électrique d'au plus  $0,7 \Omega \cdot \text{cm}^2$ .

3. Pile selon la revendication 1 ou 2, dans laquelle ladite pellicule solide (3) possède une épaisseur comprise entre 0,1 et 0,5 mm.

4. Pile selon l'une quelconque des revendications 1 à 3, dans laquelle les pellicules (31...33) constituant ledit ensemble stratifié sont placées en contact intime avec une solution acide ou neutre.

5. Pile selon l'une quelconque des revendications 1 à 3, dans laquelle les pellicules (31...33) constituant ledit ensemble, stratifié sont placées en contact intime avec une solution contenant du méthanol.

FIG. 1



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FIG. 2

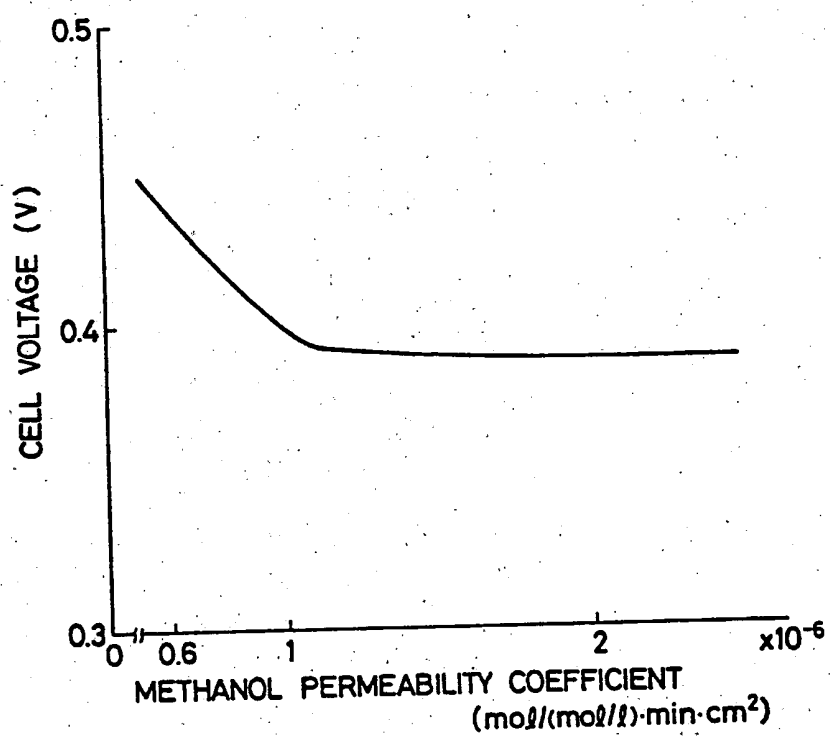


FIG. 3

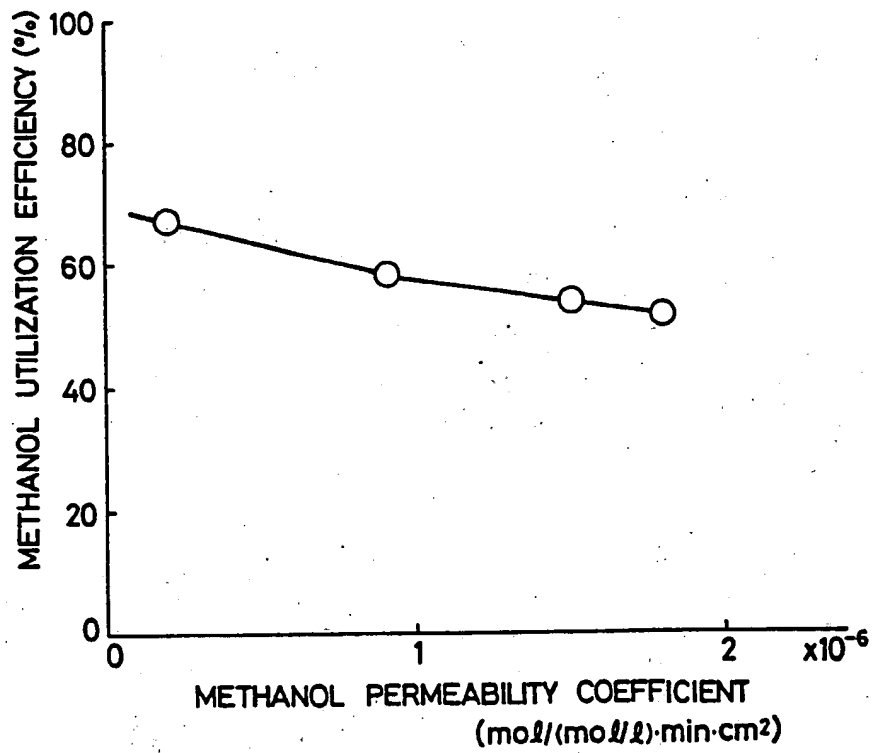


FIG. 4

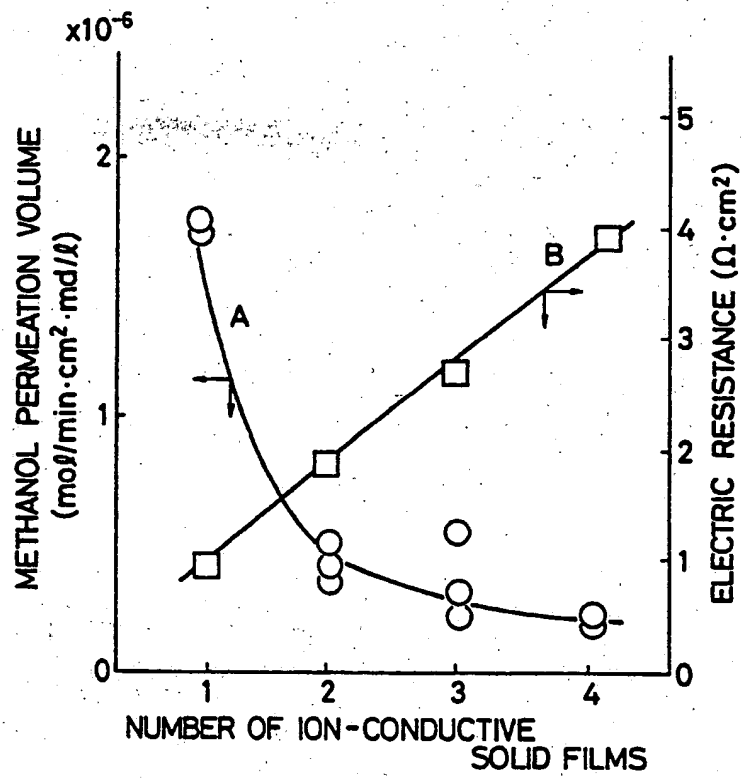




FIG. 5

